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# Infrared and electrical properties of amorphous sputtered $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$ films

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Amorphous  $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$  ( $0.61 \leq x \leq 0.73$ ) films have been deposited by sputtering in a partially reactive atmosphere. The average dielectric constant of the as-deposited films was 13.4 and 12.5 following annealing at 700 °C for 60 min in N<sub>2</sub>; both values were much lower than the single crystal values ~24 and 28 for LaAlO<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>, respectively. Leakage current densities were  $\sim 10^{-8} \text{ A cm}^{-2}$  for an applied field of 1 MV cm<sup>-1</sup> for film thicknesses  $\sim 75$  nm. Fourier transform infrared spectroscopy reveals transverse optic mode peaks at 723 and 400 cm<sup>-1</sup> and corresponding longitudinal optic modes at 821 and 509 cm<sup>-1</sup>. The density of the amorphous phase is estimated to be  $\sim 0.9$  times the crystalline density. © 2003 American Institute of Physics.

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## I. INTRODUCTION

A variety of criteria must be satisfied when choosing an alternative dielectric to replace SiO<sub>2</sub> in memory cell applications or as gate oxides in metal–oxide–semiconductor field-effect transistors (MOSFETs). The extent of the criteria, such as band offsets,<sup>1</sup> thermodynamic stability with the silicon substrate,<sup>2</sup> dielectric/Si interface quality, etc., is unquestionably the reason why dielectrics with a modest permittivity  $\sim 12$  have emerged as medium term candidates.<sup>3</sup> In essence, the solution adopted appears to be one of using a silicate base in which a high dielectric constant material is diluted, for example HfO<sub>2</sub> ( $k \sim 22$ ) in SiO<sub>2</sub> ( $k \sim 3.9$ ). The presence of the SiO<sub>2</sub> intuitively improves the compatibility of the dielectric with the Si substrate and, furthermore, renders the resultant ternary oxide amorphous up to a very high temperature which is a desirable feature since grain-boundary leakage currents frequently arise in polycrystalline films. Nitridation of the silicate films (Hf<sub>x</sub>Si<sub>y</sub>O<sub>2-z</sub>N<sub>z</sub>) further stabilizes the amorphous phase<sup>4</sup> and improves the resistance to B diffusion which is important if B-doped Si is used in the gate electrode, for example.

The Hf silicate solution will undoubtedly resolve the need of technology for an alternative MOSFET gate dielectric for a limited number of generations of devices. In the longer term, a higher dielectric constant material (say  $k \sim 22$ ) may be desirable. As a general rule,<sup>1</sup> the dielectric constant is inversely proportional to the electronic band gap so that band offset effects become significant and many high dielectric constant materials must be excluded because the barrier height to carrier injection from the Si conduction/valence bands to the insulator conduction/valence bands is too small. Ta<sub>2</sub>O<sub>5</sub> is an excellent example.<sup>1</sup> Two materials

which have acceptable dielectric constants, adequate band gaps,<sup>5</sup> and band offsets<sup>1</sup> are LaAlO<sub>3</sub> ( $k \sim 24$ ) and La<sub>2</sub>O<sub>3</sub> ( $k \sim 28$ ). Furthermore, both are predicted<sup>2</sup> to be thermodynamically compatible with Si. Note, however, that La<sub>2</sub>O<sub>3</sub> is moisture sensitive so it may not be suitable in a microelectronics processing environment. In the work reported here, the author has begun a study of the electrical and physical properties of  $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$  ( $x \geq 0.61$ ) deposited by sputtering of an LaAlO<sub>3</sub> target in a partially reactive atmosphere.

## II. EXPERIMENT

*n*- or *p*-type Si (100) 3–5 ohm cm resistivity wafers were first rinsed in HF acid then blown dry. Thin  $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$  films were deposited at room temperature by sputtering from a polycrystalline LaAlO<sub>3</sub> target using a 13.56 MHz radio frequency (rf) sputtering source (TORUS 2) with an Ar/O<sub>2</sub> gas mixture. The chamber pressure was 10 mTorr and the gas flow rates were 75 sccm for Ar and 5 sccm for O<sub>2</sub>. The typical rf power was 80 W. Assistance in exciting the plasma and increasing its density was provided via a six-antenna microwave excited electron cyclotron resonance structure; here, the frequency was 2.45 GHz and the power typically 400 W. Finally, the substrate holder and sample were biased using a 13.56 MHz rf source; a power of 40 W resulted in a substrate potential of  $-90$  V. This bias was used to provide some ion assisted deposition of the film and so densifies it. Under these conditions,  $(\text{La}_x\text{Al}_{1-x})_2\text{O}_3$  films were obtained with  $0.61 \leq x \leq 0.73$  as determined by x-ray photoelectron spectroscopy (XPS) profiling. The rate of deposition of the film was typically 1.4 nm min<sup>-1</sup>. Typical film thicknesses were between 70 nm and 100 nm. A second set of samples whose stoichiometry was not ascertained was produced by electron-beam (e-beam) evaporation using bulk LaAlO<sub>3</sub> wafers as the evaporation source. The base pressure in the chamber was  $1.0 \times 10^{-6}$  Torr and, during evaporation, an

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oxygen pressure of  $1.0 \times 10^{-4}$  Torr was used. The film thickness and refractive index ( $n$ ) for all films were determined using single wavelength (632.8 nm) ellipsometry; the film thickness was also confirmed by measurement of the Kissig fringes obtained using small angle x-ray reflectivity. Metal–oxide–semiconductor capacitor structures were manufactured using a shadow mask to define Al dots produced by thermal evaporation. The back face of the wafers was also metallized to ensure electrical contact. Capacitance–voltage ( $C$ – $V$ ) curves were measured at a frequency of 100 kHz using a Keithley 590 system. The same system was used to measure leakage current density ( $J$ ) as a function of applied voltage ( $V$ ). Prior to electrode deposition, wafers were cleaved and some samples were subjected to an anneal at 700 °C for between 10 and 60 min in N<sub>2</sub>. A set of samples without Al dots or back face metallization was used for the x-ray reflectivity studies and for Fourier transform infrared (FTIR) absorption measurements, some of these samples were annealed up to 900 °C in N<sub>2</sub> for 30 min.

### III. RESULTS

The primary objective of the experiments reported here was not to study in any detail the e-beam evaporated material, but to use it as a reference. Other authors have studied the properties of e-beam evaporated LaAlO<sub>3</sub> films,<sup>6</sup> and their films were found to be amorphous even after annealing at 700 °C for 10 min in N<sub>2</sub>. The  $C$ – $V$  and current–voltage ( $I$ – $V$ ) data reported indicated dielectric constants  $\sim 24$  and current densities of the order of  $10^{-5}$  A cm<sup>-2</sup> for an electric field  $\sim 1$  MV cm<sup>-1</sup> in annealed samples. These data were not reproducible in the e-beam evaporated material. Although current densities  $\sim 10^{-5}$  A cm<sup>-2</sup> were observed for an electric field of  $\pm 1$  MV cm<sup>-1</sup> in unannealed 80 nm thick samples, 700 °C anneals for 10 min in N<sub>2</sub> severely degraded the  $I$ – $V$  characteristic. Furthermore, unannealed samples revealed dielectric constants of only  $\sim 7.5$  and refractive indices of 1.632 at 632.8 nm; following annealing, the dielectric constant rose to  $\sim 11$  and the refractive index increased to 1.68. The author has no explanation for the discrepancy between these data and the previous authors'.<sup>6</sup>

In Fig. 1, we show typical  $C$ – $V$  and current density–electric field ( $J$ – $E$ ) data for (La<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> samples deposited by sputtering then annealed for 30 min in N<sub>2</sub> at 700 °C, the substrate was *p* type.  $E$  is simply assumed to be the applied voltage divided by the film thickness. The film thickness for this example was 75.4 nm as determined ellipsometrically. From XPS measurements, we determined  $x \sim 0.61$ . Prior to annealing, we obtained an average dielectric constant of  $\sim 11$  and a refractive index of 1.77 while these values changed to 12.5 and 1.82, respectively, following annealing at 700 °C in N<sub>2</sub> for 60 min. For other samples with  $x=0.73$ , we obtained  $k \sim 13.4$  ( $n \sim 1.75$ ) before anneal and  $k \sim 12.5$  ( $n \sim 1.78$ ) following 60 min in N<sub>2</sub> at 700 °C. We were unable to obtain samples having a dielectric constant exceeding 13.4.

Assuming an Al electrode and a substrate with the doping level  $\sim 10^{15}$  ions cm<sup>-3</sup> as we have used, the metal–semiconductor work function difference is approximately

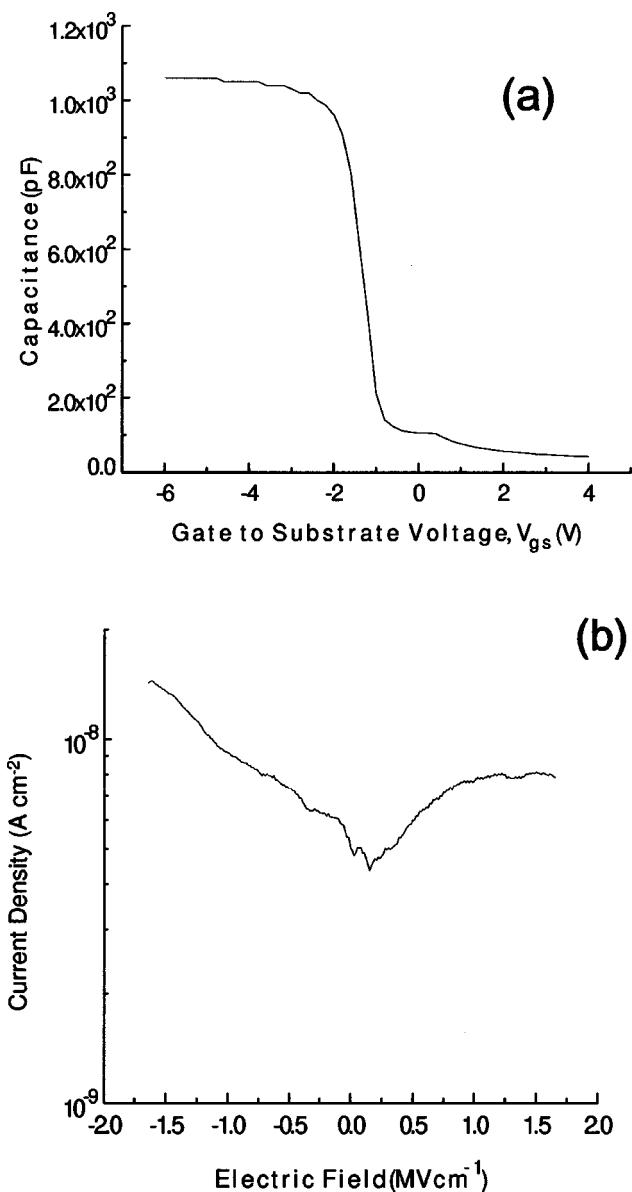


FIG. 1. (a)  $C$ – $V$  curve measured at 100 kHz in a sputter deposited sample annealed at 700 °C for 30 min in N<sub>2</sub>. (b) Current density as a function of applied electric field measured on the same sample.

−0.9 V so that, in the absence of interface state and trapped oxide charge effects, we would expect a flat-band voltage of this magnitude.<sup>7</sup> The  $C$ – $V$  curve shown in Fig. 1 is consistent with a flat-band voltage in the −1 to −2 V region suggesting that trapped charge and interface state effects are not dramatic. Repeated cycling of the  $C$ – $V$  curve evidenced little or no hysteresis at first sight. However, bias stressing followed by rapid  $C$ – $V$  measurement indicated the possible presence of mobile, positive charges in both the as-deposited and annealed films. These measurements will not be addressed here since we are primarily concerned with measurements of the dielectric constant.

In Fig. 2, we show the results of FTIR absorption spectroscopy measurements on annealed sputtered films. The samples studied were cleaved from the same wafers as used for the  $C$ – $V$  and  $J$ – $V$  measurements. The absorption spectrum observed for an unannealed film is identical to that

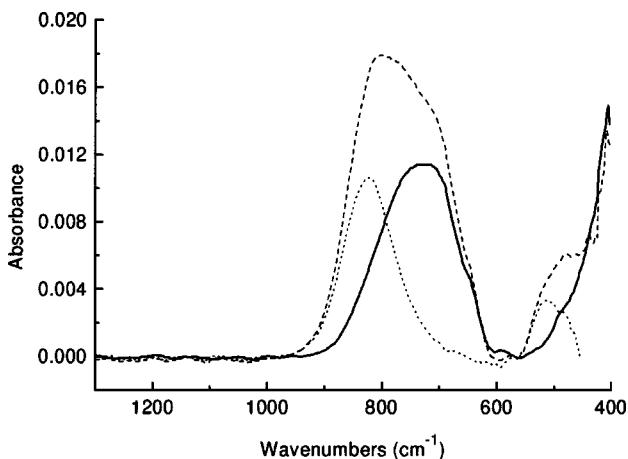


FIG. 2. FTIR spectra in samples of  $(La_x Al_{1-x})_2 O_3$  obtained by sputtering then annealing at  $700^\circ C$  for 30 min in  $N_2$ . The solid line corresponds to the normal incidence spectrum (TO modes), the dashed line is the combined TO and LO mode spectrum obtained at an angle of incidence of  $65^\circ$  and the dotted line is the LO mode spectrum obtained by subtracting the TO spectrum from the mixed mode spectrum.

found for the  $700^\circ C$  annealed film consistent with the film being amorphous even after annealing at that temperature. One curve corresponds to the normal incidence beam spectrum while another corresponds to the spectrum observed for an angle of incidence of  $65^\circ$ . Under non-normal incidence conditions both transverse optic (TO) and longitudinal optic (LO) vibrational modes are excited in the film.<sup>8</sup> We note that no absorption is seen in the region of  $1050$ – $1100\text{ cm}^{-1}$  in the normal incidence spectrum or at  $1250\text{ cm}^{-1}$  in the  $65^\circ$  incidence spectrum. Since this is the “classical” region for strong vibrational modes in  $SiO_2$ , we can conclude that there is a negligible amount of  $SiO_2$  present in the structure—in particular, at the  $(La_x Al_{1-x})_2 O_3/Si$  substrate interface. We can, therefore, reasonably suggest that the low dielectric constant we have measured in the amorphous  $(La_x Al_{1-x})_2 O_3$  films does not result from the presence of an interfacial  $SiO_2$  film which would reduce the overall dielectric constant. Consequently, the low dielectric constant is intrinsic to the nature of the deposited amorphous film. Also shown in Fig. 2 is the curve resulting from the subtraction of the normal incidence data from the  $65^\circ$  incidence spectrum. The spectrum is indicative of the pure LO modes and this allows one to ascertain that the amorphous film peaks occur at approximately  $821$  and  $509\text{ cm}^{-1}$ . The pure TO mode peaks occur at  $723$  and  $400\text{ cm}^{-1}$ , respectively, although little precision can be attributed to the latter value since the complete peak shape with its maximum is not resolved. In Fig. 3, we show the normal incidence FTIR spectrum for a sputtered film annealed for 30 min in  $N_2$  at  $900^\circ C$ . We include the  $700^\circ C$  annealed spectrum for comparison. The higher-temperature annealing has clearly transformed the film and an intense peak centered upon  $912\text{ cm}^{-1}$  has appeared. This peak position is rather similar to that observed<sup>9</sup> in the annealing of  $La_2O_3$  films on Si which is attributed to O vibrations in Si–O–La linkages. It clearly suggests that  $900^\circ C$  annealing of  $(La_x Al_{1-x})_2 O_3$  on Si results in an interaction of the Si

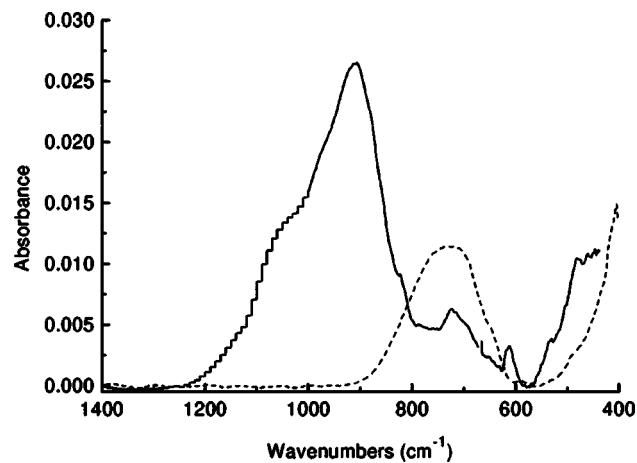


FIG. 3. Normal incidence FTIR spectra for a  $(La_x Al_{1-x})_2 O_3$  sample deposited by sputtering then annealed at  $700^\circ C$  for 30 min in  $N_2$  (dashed line) or  $900^\circ C$  for 30 min in  $N_2$  (solid line). In the latter case, one observes a strong peak around  $912\text{ cm}^{-1}$  which may be due to Si–O–La linkages and a peak around  $1050\text{ cm}^{-1}$  due to Si–O–Si linkages. There has clearly been a reaction between the deposited film and the Si substrate.

with the film. This is not anticipated on the basis of thermodynamic calculations of phase stability.<sup>2</sup>

#### IV. DISCUSSION

In Fig. 4, we schematically show the dielectric constant as a function of  $x$  in  $(La_x Al_{1-x})_2 O_3$  compounds. We include a point for  $Pr_2O_3$  which is characteristic of most of the lanthanide sesquioxides, i.e.,  $k \sim 14$ . The  $x$  values for the samples we have prepared would suggest that they should have dielectric constants lying somewhere between the known  $LaAlO_3$  and  $La_2O_3$  values. It would appear that the data we have obtained in fact lies reasonably on an interpolation between  $Al_2O_3$  and  $Pr_2O_3$  while the crystalline phase lanthanide values ( $LaAlO_3$  and  $La_2O_3$ ) are significantly

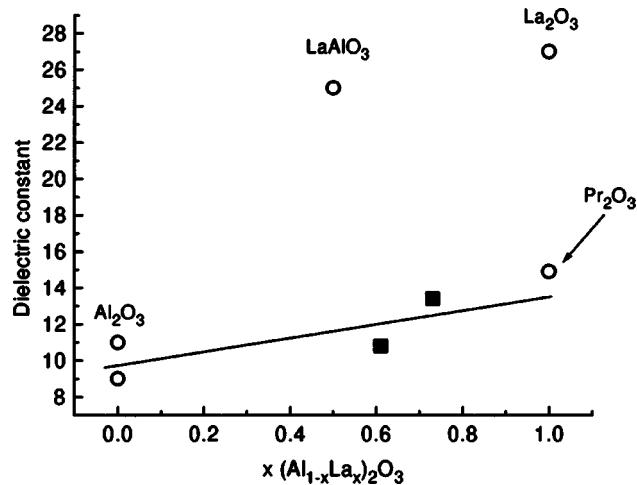


FIG. 4. A plot of the dielectric constant as a function of  $x$  in amorphous and crystalline  $(La_x Al_{1-x})_2 O_3$  compounds, the value for  $Pr_2O_3$  is included since it is typical of most lanthanide sesquioxides.  $La_2O_3$  is unusually large due primarily to larger molar polarizability.

higher. We must, therefore, address the issue of the discrepancy in dielectric constants between the deposited amorphous materials and crystalline forms.

In order to give further credibility to the values of a dielectric constant that we have measured, we can appeal to the infrared absorption data. The low- [ $k(0)$ ] and high- [ $k(\infty)$ ] frequency dielectric constants are related to the TO and LO vibrational frequencies through the Lyddane–Sachs–Teller relationship.<sup>10</sup> When various modes of vibration are present, this may be written:<sup>11</sup>

$$k(0)/k(\infty) = \Pi \omega_j^2 \text{LO} / \omega_j^2 \text{TO}, \quad (1)$$

where the product is over all vibrational modes  $\omega_j$ . We assume that the high-frequency dielectric constant is given by  $k(\infty) = n^2$ , where  $n$  is the refractive index. For the crystalline phase of LaAlO<sub>3</sub>, the TO and LO vibrational mode frequencies have been calculated<sup>12</sup> and, using the refractive index value<sup>13</sup> of 2.04 in Eq. (1), we ascertain  $k(0) = 29$  which is close to the measured value<sup>14</sup> ~24. If we use the TO and LO vibrational frequencies, we have measured for the amorphous (La<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> films together with the refractive index measured at 632.8 nm, we deduce  $k(0) = 6.92$ . This value is significantly lower than the value we have measured of 13.4, but it has the merit that it is closer to the experimental amorphous dielectric constant than that expected for crystalline material (assuming that for the samples we have studied with  $x \geq 0.61$ , the dielectric constant of a crystalline material would lie between LaAlO<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> values). It is also possible that there are vibrational modes and splittings that we have not included in the calculation based upon Eq. (1) (for frequencies less than 400 cm<sup>-1</sup>) and this needs to be further explored using an FTIR capable of measuring at lower wave numbers.

The experimental value of  $k(0) = 13.4$  for (La<sub>0.73</sub>Al<sub>0.27</sub>)<sub>2</sub>O<sub>3</sub> remains, then, becomes considerably lower than the crystalline values of 24 for LaAlO<sub>3</sub> or 28 for La<sub>2</sub>O<sub>3</sub>. Could one explanation be that the deposited films are porous? We note first that ion beam assistance (sample bias) was used during deposition and, that secondly, the effects of annealing on the dielectric constant were rather small suggesting that the film had reached some limiting dielectric constant value. Independent confirmation of the correct value is required.

In the simplest interpretation of the dielectric constant, it may be determined through the Clausius–Mossotti equation:<sup>10</sup>

$$(k-1)/(k+2) = (4\pi/3)\alpha/V_m, \quad (2)$$

where  $V_m$  is the molecular volume and  $\alpha$  the molecular polarizability. For the crystalline phases, we obtain  $\alpha/V_m = 0.21$  for LaAlO<sub>3</sub> and  $\alpha/V_m = 0.215$  La<sub>2</sub>O<sub>3</sub> while for the amorphous phase of (La<sub>0.73</sub>Al<sub>0.27</sub>)<sub>2</sub>O<sub>3</sub>, using our  $k$  value, we obtain  $\alpha/V_m = 0.19$ . If we make the simplified assumption that the molar polarizability does not change with density between the crystalline and amorphous phases, then we can very approximately conclude from the ratio of the  $\alpha/V_m$  values that the ratio of the densities,  $\rho_{\text{amorph}}/\rho_{\text{crystalline}} \sim 0.9$ . In simple terms, our experimental dielectric constant is consistent with the density of the amorphous phase of

(La<sub>0.73</sub>Al<sub>0.27</sub>)<sub>2</sub>O<sub>3</sub> being ~90% of the crystalline phase value for LaAlO<sub>3</sub> or La<sub>2</sub>O<sub>3</sub>. Interestingly, if one uses a similar analysis for the case of amorphous and crystalline Al<sub>2</sub>O<sub>3</sub>, then one also concludes that  $\rho_{\text{amorph}}/\rho_{\text{crystalline}} \sim 0.9$ .

One may also take into consideration the refractive index measurements using the well-known Lorentz–Lorenz equation:

$$(n^2 - 1)/(n^2 + 2) = (4\pi/3)\alpha_{\text{opt}}/V_m, \quad (3)$$

where  $\alpha_{\text{opt}}$  is the optical frequency molecular polarizability. Assuming the measured value of the refractive index for our films is typically ~1.8 following annealing, then we deduce  $\rho_{\text{amorph}}/\rho_{\text{crystalline}} \sim 0.87$  using the known<sup>13</sup> refractive index for LaAlO<sub>3</sub> and an extrapolated value<sup>15</sup> ~2.0 for La<sub>2</sub>O<sub>3</sub>. This is sufficiently close to the value of the ratio determined from dielectric constant measurements given herein to give strong support to the hypothesis that amorphous (La<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> with  $x > 0.5$  is approximately 10% less dense than its crystalline counterpart.

Several interesting scientific issues arise related to the network structure of amorphous (La<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> and the amorphous-to-crystalline phase transformation. In e-beam evaporated material we have found, as have other authors,<sup>6</sup> that the amorphous phase is stable even after 700 °C annealing. Similarly, the rf sputtered material we have studied here was also stable to high-temperature anneals. rf sputtered (La<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> deposited on substrates heated to 850 °C was also found to remain amorphous if the O<sub>2</sub> pressure in the reactor was maintained higher than ~0.1 mTorr.<sup>16</sup> It is clear from these results that the amorphous phase is very stable. Nuclear magnetic resonance measurements<sup>17</sup> on (La<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> have evidenced the presence of AlO<sub>4</sub>, AlO<sub>5</sub>, and AlO<sub>6</sub> network units in numbers which depend upon both the relative concentrations of Al and La and the annealing temperature. In the amorphous stoichiometric (LaAlO<sub>3</sub>) phase, it is found that substantial numbers of AlO<sub>4</sub> structures are present even at temperatures as high as 600 °C. One is then tempted to ask whether the amorphous stability is related to this unusual bonding. Similar structures are found in the results of calculations<sup>18</sup> of the network in Al<sub>2</sub>O<sub>3</sub>, where it is suggested that the lower density of the amorphous network (as compared to the crystalline phase) may in part result from the presence of nominally undercoordinated Al's. In consequence, we suggest that the lower density of the amorphous (La<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> samples studied here as compared to the crystalline phases LaAlO<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> is due to a network coordination effect rather than, for example, the presence of porosity which might also be invoked in explaining reduced network density. This coordination effect may be due in part to the nonstoichiometry of our films (i.e., neither LaAlO<sub>3</sub> nor La<sub>2</sub>O<sub>3</sub>). It is clearly possible that stoichiometric phases would have better atomic packing leading to higher densities as in the case, for example, of most of the SiO<sub>2</sub> crystalline polymorphs when compared with amorphous SiO<sub>2</sub>. Measurements to confirm the coordination in the thin films would be valuable.

## V. CONCLUSION

If the results presented here are confirmed, it would appear that amorphous  $(La_xAl_{1-x})_2O_3$  with  $x > 0.5$  is less dense than its crystalline counterpart, and this results in a dielectric constant that is significantly reduced. The primary advantage of using this material is then lost since other Si compatible oxides with similar dielectric constants are available in the form of  $Hf_xSi_yO_{2-z}N_z$ . Furthermore, we have established that high-temperature annealing results in an interaction between the  $(La_xAl_{1-x})_2O_3$  and the underlying Si even though thermodynamics failed to predict this. On this basis, there would appear to be no salient feature which drives one to use  $(La_xAl_{1-x})_2O_3$  rather than other already available dielectrics.

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